

# **ZEOLITE ADDITIVE FOR RUBBER AND PLASTIC**

## **CROSS REFERENCE TO RELATED APPLICATIONS**

5

This application is a continuation-in-part of, and claims the priority date of, patent application serial number 09/552,360 filed April 10, 2000, which is a continuation-in-part claiming the priority date of patent application serial number 09/678,162 filed February 3, 2000.

10

## **FIELD OF THE INVENTION**

15

This invention relates to rubber and plastic items containing zeolites, and methods for manufacturing such items. More specifically, the invention includes methods and apparatus that use absorbent and adsorbent materials in a shoe lining; and most particularly, this invention relates to methods and apparatus that provide shoe liners, sole inserts, and similar rubber and plastic apparatus, and methods to create such absorbent rubber and plastic.

20

## **BACKGROUND OF THE INVENTION**

25

Rubber and similar products, such as neoprene, urethane, and the like are ubiquitous in modern life. They are used in thousands of places considered entirely normal today. The properties of rubber, including elasticity, the ability to be easily foamed, and the ability it was named for, the ability to erase pencil lines, have been exploited thoroughly in modern life. Of course, since World War II and after thousands of synthetic latexes have been formulated to fill various specialized niches. However, despite all these improvements, rubber is poor at the absorption of moisture and water.

30

Rubber is normally quite water repellent. It can be made to absorb moisture if it is foamed, one example being kitchen sponges, but the moisture goes to the interstices of the rubber rather than into the rubber composition itself. It would be advantageous to

have a rubber composition that absorbed at least some moisture as well as odor causing components, such as ammonia and the like.

One example of a use for this would be for use in the inner soles placed in athletic shoes and the like. Feet, as other parts of the body, produce perspiration. This creates a continuous source of moisture on the interior of shoes. Since a foot confined in a shoe has little opportunity to shed this moisture, there is a problem of keeping the feet fresh. A variety of methods, for example powders and the like, have been tried to keeping shoes smelling fresh and clean. One other method of preparing shoes for wearing includes the addition of a shoe insert to the interior of a shoe. These inserts frequently have ingredients that allow the foot and the

One potential solution is the addition of zeolites to the rubber composition. Zeolites are alumino-silicates having complex crystalline structures that can allow the crystalline structure to absorb small molecules, such as water ammonia. Zeolites are also used in cracking catalysts for petroleum processing and similar uses. Again, the reason for such uses is that zeolites can exclude molecules based on the molecular size of the molecule. They can exclude in the micro range ( $<2\text{nm}$ ) or the meso-range ( $2 - 20\text{ nm}$ ).

There are families of zeolites or molecular sieves as they are frequently known, are defined by their molecular structures, in particular their crystalline structures, and their chemical compositions. One important family of zeolites is alumino-silicates having the general empirical formula of  $M_{2n}O \cdot Al_2O_3 \cdot y \cdot SiO_2 \cdot w \cdot H_2O$ , where  $y$  is 2 or greater,  $M$  is the charge of a balancing action, such as sodium, potassium, magnesium and calcium,  $n$  is the action valance, and  $w$  represents the number of moles of water contained in the zeolitic voids.

Of the 120 or so zeolites known to exist, about 50 are naturally occurring and the rest are synthetic. Commercially available naturally occurring zeolites include chabazite, erionite, mordenite, and clinoptilolite. Other zeolites included faujasite, phillipsite, zeolite A, zeolite L, Zeolite Y, zeolite X and ZSM-5. All these zeolites vary by the

particulars of their cage structure and the pore sizes, and therefore, vary in the molecules that can be excluded by the zeolites. Many zeolites are mined directly from the earth, and these are less pure than synthetic zeolites containing dirt, clays, and other associated material from the earth. However, mined zeolites work well in this application, as long as they are ground to at least as small as 300 mesh. And that is the source of their problem for use in rubber. If the zeolite is added just as mined, the final product will be brittle, and will not absorb water or moisture.

### SUMMARY OF THE INVENTION

This invention provides rubber or plastic compositions are made by adding a zeolite that has been dried and crushed to an average size of less than 300 mesh. In general, throughout this application, references to rubber are considered to include known plastic materials in addition to known rubber materials. The rubber composition may be foamed and can be made from a variety of materials, including natural or synthetic latex, or polyurethane. These compositions allow rubber to be moisture and odor absorbent, even if the rubber is not foamed. They can be used for a wide variety of products, including, as examples, shoe inserts, bed pads, gasket materials, computer mouse pads, seating cushions, and the like. The rubber of the present invention can be easily regenerated by heating the rubber to between about 50°C and 150°C.

One aspect of this invention is a rubber composition comprising: between about 10 weight percent and 90 weight percent of a rubber material selected from the group consisting of natural rubber and synthetic rubber; between about 80 weight percent and 1 weight percent of a zeolite that has been dried at between 50°C and 150° for between about one and twenty four hours, prior to manufacturing, and ground to a size smaller than 300 mesh; and at least enough stabilizers and vulcanizers to stabilize the composition.

Another aspect of this invention is a method of making a rubber composition comprising: adding to a rubberized compound in its liquid state, a zeolite that has been dried at

between 50°C and 150° for between about one and twenty four hours, and ground to a size smaller than 300 mesh and at least one stabilizer; molding the liquid material; and shaping the solidified material.

- 5 Yet another aspect of this invention is a method of freshening the inside of shoes comprising: placing a renewable insert comprising a rubberized matrix and a zeolitic odor absorbent, said zeolitic odor absorbent containing zeolite that has been dried at between 50°C and 150° for between about one and twenty four hours, and ground to a size smaller than 300 mesh in the inside of the shoe.

10

#### DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

- Rubber, either natural or synthetic, or rubber like materials, such as polyurethane, can be formulated with zeolite as an additive. The rubber or Plastic can be solid or foam, either  
15 open cell or closed cell foam. The resulting formulation has unusual properties including reduced curing time and the ability of the rubber formulation to absorb moisture, even in formulations that are not foam rubber. The composition including between about 10 weight percent and 90 weight percent of a rubber material selected from the group consisting of natural rubber and synthetic rubber; and between about 85 weight percent  
20 and 1 weight percent of a zeolite. The composition may also contain stabilizers, vulcanizers, and other ingredients to produce a superior rubber product.

- The rubbers are either natural or synthetic. Natural rubber is the product of rubber trees and is mostly isoprenes. Synthetic rubbers include polyisoprene, styrene butadiene,  
25 nitrile rubbers, butyl rubbers, ethylene propylene terpolymers, silicone rubbers, neoprenes, polysulfide, poly acetyl, eperchloride, fluorelastomers, hypalon, halogenated butyl, polyurethanes, and thermoplastic rubbers. Stabilizers can include those selected from the group consisting of alkaline earth carbonates, and other alkali metal carbonates and alkaline earth carbonates, and other alkali metal bicarbonates. For example, the  
30 composition of the stabilizer of alkaline earth carbonates is in the form of limestone, calcium carbonate, magnesium carbonate, sodium carbonate, potassium carbonate,

sodium bicarbonate and potassium bicarbonate. Vulcanization ingredients include sulfur, TMTD (tetramethyl thioperoxide carbonic diamide or Thiran) and a host of others. Other additives include vulcanizer accelerants, peroxide cures, and retarders. For example, group II B metal oxides such as zinc oxide; Aflux 16; TMTD; MBT (2-

5 Mercaptobezothiozole); and DPTT can be added. Various other ingredients can be included in a rubber formulation, for example, diethylene glycol, ethylene glycol, and other poly-ethers. The color can be modified by adding, for example, MT Black. Paraffinic oil can give the final composition resilience and flexibility. Although new additives are being found, the technology of rubber formulation is quite old, and  
10 comprehensive list of suitable additives can be found in Kirk-Othmer's *Concise Encyclopedia of Chemical Technology* (and the parent *Encyclopedia of Chemical Technology* in its various editions as well) 1985, John Wiley and Sons, New York under articles for Rubber and Rubber Compounds, which disclosure is incorporated in full herein.

15

Nearly any zeolite can be used in this invention. Zeolites, also known as molecular sieves, having a pore size ranging from about 2 Angstroms to 100 Angstroms are preferred, those having pore sizes between about 3 angstroms to 20 Angstroms are particularly preferred. These zeolites can be used, as can any naturally or synthetically  
20 made zeolite including chabzite, erionite, mordenite, clinoptilolite, faujasite, phillipsite, zeolite A, zeolite L, Zeolite Y, zeolite X and ZSM-5. The key to an acceptable zeolite is that the pore size that characterizes the zeolite be of a size sufficient to capture water molecules. One particularly preferred zeolite is clinoptilolite.

25 Surprising and unanticipated features of this invention are twofold. First, the zeolite used must be dried before it is added to the rubber composition. The drying of mined zeolite is easily accomplished by exposing the mined zeolite to a temperature between about 50°C and 100°C, preferably between about 60° and 150°C and most preferably between 75°C  
30 200°C for between one and twenty four hours, preferably between three and eighteen hours and most preferably between four and twelve hours. Zeolite so processed will be referred to as "dried zeolite" herein; although it will be realized by those having even a

mere passing knowledge of the art that the starting material is neither wet nor does it contain visible moisture. Any and all moisture in the mined product is contained within the interstices of the zeolitic crystalline structure. Second, the zeolite, whether it is natural or synthetic, must be ground to a mesh size of no larger than 300 mesh (approx. 0.08 mm in diameter); that is the average diameter of the particles useful in this invention must have diameters of no more than 300 mesh. Zeolite so ground or crushed will be referred to as "crushed zeolite" herein.

Rubber compositions that contain undried zeolite do not cure well, and may deform after curing. Moreover, zeolite having mesh sizes as small as 250 mesh (0.1 mm) do not give satisfactory results. It is preferred that the zeolite be crushed before it is exposed to the drying.

The zeolite used in this invention must be dried before processing to achieve the advantages of this composition. In most embodiments, the zeolite is preferably ground to at least a 250 grid, more preferably a 300 grid, and most preferably to at least a 325 grid. However, in some embodiments even smaller grid sizes ranging between 250 and 350 grid or smaller may be preferred.

One of the great advantages of the composition of this invention is that the life of plastic and rubber is significantly extended.

Products made using the method of this invention and the products of this invention may be tested several ways using standardized tests used to test rubber and plastic products. First, the product of this invention has superior curing properties—that is the product will cure as it is being made faster than either rubber or rubber with larger zeolite additives; and second, the product of this invention has superior moisture retention properties.

This invention can provide a composition that can easily absorb moisture into rubber, as the rubber incorporating dried and crushed zeolite is no longer hydrophobic. This invention can be used for a very wide variety of items including, but not limited to, shoe

inserts, bed pads, gasket materials, computer mouse pads, seating cushions, tires, and the like. There is no limitation to the uses for this invention.

5 It can be used for hoses, foam rubber can be made either open cell and closed cell, rubber  
pipes, hospital pads, mattress pads, shoes, particularly shoes for sports, tennis, running,  
walking jogging, it can be made with bi-directional composites, leather shoe liners, shoe  
soles, heels, shoe inserts for tennis shoes, hockey shoes, ski shoes and the like, for  
10 injected molded rubber parts, filled and non filled with reinforcement materials, rubber  
belts, fan belts, tires reinforced by web material, and non reinforced, tires, industrial and  
automobile gaskets, valves, aircraft parts, and roof liners. It can be used in sporting  
goods including but not limited to tennis balls, baseballs, footballs, soccer, wet suits, golf  
balls, gloves, protective pads, skis, bats, helmets, liners for sports equipment and the  
like. Further uses include rope, cooking utensils, storage tanks, pump propellers, air  
15 bladders, shocks absorbers and as clothing liners or as a component of the fabric  
incorporated into fabric. It can be formed by various extruded rubber methods, or using  
compression molding. An additional possible use includes use of a membrane formed in  
accord with the invention as a cell membrane in hydrogen energy cells. For example,  
zeolite added to naphthalene has been found to improve the durability of such membranes.  
20 Some compositions of the invention exhibit good coefficients of friction for gripping  
surfaces, which may be useful when the compound is used in tires and shoe soles.

The composition of this invention can be used to absorb moisture, while strengthening  
rubber and plastic, preventing electrolysis, slowing the aging process of the rubber and  
25 plastic articles, and reducing cycle time in manufacturing of plastic and rubber. Shoes,  
especially athletic shoes, usually have three components. The first one is the shoe sock  
that surrounds the inner shoe, usually made of foam rubber or EVA plastic foam. The  
second one is the inner sole that is on the inside of the bottom next to the foot, and it is  
usually made of EVA Plastic and is foam. The outer sole is usually rubber.

30

An inner shoe sock could also be used on leather shoes to prevent the leather from cracking and deteriorating as it ages.

5 There are preliminary indications that some composition of this invention eliminate or reduces electrolysis. This effect is noticed in shoes using EVA plastic foam in the sock where heat and moisture create an electrolysis process.

10 This invention allows the absorption of other components that may be undesirable as well, such as, ammonia and urea (particularly, in the case of shoes), hydrogen sulfide, methane, and alcohols, particularly methanol, ethanol, and the like.

Once water and other substances have been absorbed into the rubber, the rubber will lose its ability to absorb more moisture. However, the material of this invention can be regenerated by heating it to between about 50°C and 150°C for between about 30 minutes  
15 and 5 hours. Indeed, for many applications, the rubber can be regenerated by placing it out side in the sunlight for between about 30 minutes and eight hours.

One example embodiment of products that can be made using this invention are shoe inserts. A shoe can be kept fresh by using components that contain at least some zeolite.  
20 Such components include inserts, that is removable pads for the foot to rest on disposed within the shoe, and linings, which are not removable. The zeolite absorbs odors and can then release these odors when the shoe insert is removed for airing out. Usually, just the act of removing the shoe from the foot will provide at least some airing of the insert, even if it is not removed from the shoe.

25 The insert may be made of rubber or synthetic rubber, poly urethane, neoprene, and the like, and the zeolite is added as to the rubber mixture formulation. Between 1 weight percent and 85 weight percent of the formulation of the shoe insert will be zeolite. The balance of the mixture will be a mixture of between 25 weight percent and 75 weight  
30 percent rubber material and between 75 weight percent and 25 weight percent of a stabilizer. Preferred stabilizers include calcium and other alkaline earth carbonates,



sodium and other alkali metal carbonates and bicarbonates. Similarly, sulfates, silicates, aluminate and the like can be used as the stabilizer for the insert composition of the shoe. It should be realized that the exact composition of the stabilizer is not critical to this invention, and any composition conventionally used for stabilization of rubber compositions can be beneficially used in the invention.

The insert of the present invention can be made to fit inside a shoe, for example, in an athletic shoe or in an orthopedic shoe. Although, the insert will generally be used inside and on the bottom surface of an enclosed shoe, open shoes such as sandals, and the like can beneficially use the insert of the present invention. It should also be realized that the insert may be for the portion of the shoe between the shoe and the foot. The present invention can be used to freshen shoes and feet or to provide a means of providing a hygienic environment for the advancement of foot care for such diseases as athletes foot, and similar ailments.

It will be appreciated that the insert of the present invention can be made as a single molded piece or a plurality of pieces bonded together to form a more cushioned insert or a form fitting piece—indeed such form fitting pieces can be custom molded to fit a particular foot inside a particular shoe. It will also be realized that the rubber shoe insert of this invention containing zeolite can be used as a top layer to any other type of composition being used as a shoe insert.

## EXAMPLES

The examples shown herein are exemplary of the invention and are not intended to limit the scope of the appended claims in any manner.

### Example 1

This example shows how to make a composition suitable for the insert of the present invention.

100 grams of naturally occurring chinoptilolite is ground to 300 mesh and then the fine  
5 particles are dried at 100°C for six hours before being added to a 100 grams of rubber in  
liquid state. The mixture is stirred for fifteen minutes then approximately 50 grams of  
calcium carbonate is added to the mixture.

The mixture is made into a long band, solidified and the shoe inserts are cut from the  
10 cooled band.

Similarly; other zeolite that can be substituted include chabzite, erioite, mordenite,  
chinoptilolite, faujasite, philpsite, zeolite A, zeolite L, Zeolite Y, zeolite X and ZSM-5.  
Similarly; other polymers that can be substituted include latexes made from isoprenes,  
15 polisoprenes, styrene butadienes, nitrile rubbers, butyl rubbers, ethylene propylene  
terpolymers, silicone rubbers, neoprenes, polysulfides, poly acetyls, eperchlorides,  
fluoroelastomers, hypalons, halogenated butyl, polyurethanes, and thermoplastic rubbers.  
The compositions can be hard or foamed.

20 Similarly; other stabilizers include sodium carbonate, magnesium carbonate and  
potassium carbonate.

### Example 2

25 The composition of claim one is cast in a mold the size and shape of the shoe sole. The  
material in the mod is ready for use within fifteen minutes of being placed in the mold.

### Example 3

30 In an alternative to Example 2, the composition of claim 1 may be formed as a single  
sheet, and inserts the size and shape of shoe inserts cut from the sheet.

#### Example 4

Alternative compositions can be made by mixing ingredients.

5

Compound A, compound B, and compound C were made by mixing the ingredients together while liquid and slowly cooling the composition formed. The compounds were made. The amounts of ingredients are listed in TABLE 1. The composition was foamed to make an open cell foam rubber. The various compositions were then tested.

10

Similarly, non-foam rubbers and closed foam rubbers may be made using the formulations listed above.

15

Similarly, latexes made from isoprenes, polyisoprenes, styrene butadienes, nitrile rubbers, butyl rubbers, ethylene propylene terpolymers, silicone rubbers, neoprenes, polysulfides, poly acetyls, eperchlorides, fluoroelastomers, hypalon, halogenated butyls, polyurethanes, and thermoplastic rubbers synthetic rubbers, may be substituted for the rubber, BUNA, of the formulations listed above.

20

Similarly, accelerants, stabilizers, retarders and the like may be added to the formulations listed above to achieve the desired results.

TABLE 1

## ZEOLITE FORMULATIONS (amounts expressed as grams of ingredient)

	INGREDIENTS	COMPOUND A	COMPOUND B	COMPOUND C
5	BUNA EPT 6470 P	100.00	100.00	100.00
10	ZINC OXIDE	5.00	5.00	5.00
	AFLUX 16	2.00	1.50	1.50
	TMTD	.50	.50	.50
15	MBT	1.50	1.50	1.50
	SULFUR	1.50	1.50	1.50
20	DPTT	.75	.75	.75
	DIETHYLENE GLYCOL	2.00	2.00	2.00
25	MT BLACK	5.00	5.00	5.00
	GROUND	100.00	50.00	25.00
	LIMESTONE			
30	ZEOLITE (dried and ground to 300 mesh)	100.00	150.00	200.00
35	PARAFFINIC OIL	100.00	100.00	100.00

#### Example 5

This example shows the properties of the Compound A made in Example 4

5

Compound A, with 100.00 grams of naturally occurring and mined clinoptolite, a zeolite, which was dried and crushed as noted, was made and tested. The compound was formed and cured in less than two thirds of the time it took for rubber compound to cure. The compound had good abrasion resistance, and shape recovery after stretching.

10

#### Example 6

This example shows the properties of the Compound B made in Example 4.

15 Compound B, with 150.00 grams of naturally occurring and mined clinoptolite, which was dried and crushed as noted, was made and tested. Although this compound was better than rubber alone, the extra zeolite gave a composition that had slightly less good abrasion resistance than the composition of Example 5, although it was still well within the acceptable range. It also had slightly less good shape recovery.

20

#### Example 7

This example shows the properties of the Compound C made in Example 4.

25 Compound C, with 200.00 grams of clinoptolite, failed both tests.

#### Example 8

This example shows the regeneration of the rubber of this invention that has absorbed  
30 water.

A sample of rubber made as in example 5 is used as a shoe insert. After a day of use, the insert is taken from the shoe and set out in the sunlight for eight hours. The shoe insert is now essentially moisture free, and can be used again.

## 5 Example 9

This example shows the properties of the compound A made in Example 4.

10 Compound A, with 100.00 grams of naturally occurring and mined clinoptolite, a zeolite, but which was not dried and was crushed only to 200 mesh, was made and tested. The compound was formed but took slightly more time to cure than the rubber

composition alone. The compound had poor abrasion resistance, and shape recovery after stretching.

15

This invention has been described by reference to specific embodiments and examples thereof. Various modifications, changes and alterations of this invention will naturally suggest themselves to those skilled in the art. It is intended that all such modifications, changes and alterations of the invention be encompassed by the appended claims.